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IN THE US PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF
Hidetaka Oka et al.
SERIAL NO. 09/734,635
FILED: December 12, 2000
FOR: Photosensitive Resin Composition

GROUP ART UNIT: 1752
EXAMINER: Yvette M. Clarke

Commissioner of Patents and Trademarks
Washington D.C. 20231

DECLARATION UNDER RULE 132

I, Hidetaka Oka, a citizen of Japan and presently residing in 34-5, Suenari-cho, Takarazuka City, Hyogo Pref., Japan, hereby declare:

That I was awarded the degree of Master of Chemistry by Osaka Prefecture University, Japan, in 1990; the degree of Bachelor of Chemistry by Osaka Prefecture University in 1988.

That I have been employed by Ciba Specialty Chemicals Inc. (former CIBA-GEIGY AG), Japan, as a chemist since 1990, and presently hold the position of a researcher, R&D Application Group, TC Electronic Materials, Coating Effects Segment.

That I have been engaged in the development of photoinitiators for Ciba Specialty Chemicals Inc. in the field of radiation curing since 1996.

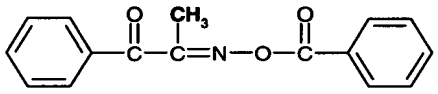
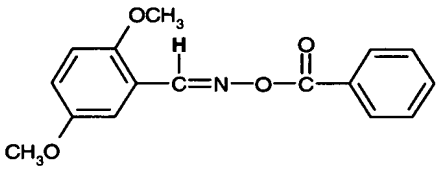
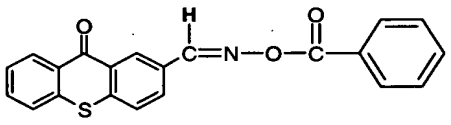
That I am the author of the following technical articles relating to the same or closely related field of research:
Hidetaka Oka, et al., Proc. RadTech Asia '99, 126 (1999).

That I am inventor of the following US Patents relating to the same or closely related field of research: US Patents Nos. 6,022,906 and 6,057,380.

That I'm familiar with U.S. Patent Application Serial No. 09/734,635 to Hidetaka Oka et al.

It was the object of the experiments to show that "aldoxime" compounds as disclosed in U.S. Patent Application Serial No. 09/734,635 are better suited as photointiators in the photoresist applications according to the invention than the corresponding "ketoxime" compound of Laridon, US Patent No. 4,282,309.

The following compounds were compared:

| Compound according to "Laridon", US Patent 4282309, col. 3, compound (A) | Compounds according to application Serial No. 09/734,635 |
|---|---|
|  A |  B1  B2 |

Experimental procedure

A photocurable formulation for a sensitivity test is prepared by mixing the following components:

| | |
|---|---|
| 200.0 parts by weight | of acrylated acrylcopolymer ($^{RTM}$ACA200M, provided by Daicel Chemical Industries, Ltd., the solid content is 50% by weight) |
| 15.0 parts by weight | of dipentaerythritol hexaacrylate (DPHA, provided by UCB Chemicals), |
| 100.0 parts by weight | of acetone |

To that mixture 2% (based on the solid content) of the photoinitiator to be tested are added and stirred. All operations are carried out under yellow light. The formulations are applied to an aluminum plate. The solvent is removed by heating at 80 C° for 15 minutes in a convection oven. The thickness of the dry film is 25 µm. To this coating an acetate film is applied, over which a standardized test negative with 21 steps of different optical density (Stouffer step wedge) is placed. The sample is covered with a second UV-transparent film and pressed onto a metal plate by means of vacuum. Exposure is carried out in a first test series for 40 seconds, in a second series for 80 seconds and in a third series for160 seconds, using a 3 kW metal halide lamp (ORC, model SMX 3000) at a distance of 60 cm. Following exposure, the cover films and the mask are removed and the exposed film is developed with 1% sodium carbonate aqueous solution for 180 sec. at 30°C by using a spray type developer (Walter Lemmen, model T21). The sensitivity of the initiator system used is characterized by indicating the highest step number which remained (i.e. polymerized) after developing. The higher the number of steps, the more sensitive is the system tested.

Results:

| Compound | Number of steps reproduced after exposure time of | | |
|---|---|---|---|
| | 40 sec. | 80 sec. | 160 sec. |
| A | 2 | 4 | 6 |
| B1 | 4 | 7 | 9 |
| B2 | 5 | 6 | 8 |

Discussion of the results

The results clearly show that this is a considerable improvement, unexpected in its extent, and highly valuable in resist technology.
Considering the reactivity results which are given in terms of the highest densitiy step of a Stouffer wedge effecting cure of the underlying photopolymer film, it should be noted that curing speed (or inverse curing time) does not increase linearly with the number of cured steps. Following relationsship holds:

$$s(1)/s(2) = 2^{0.5[n(1)-n(2)]}$$

n(1), n(2) = highest step number after exposure times 1 and 2
s(1), s(2) = curing speed corresponding to exposure times 1 and 2

Example:

| increase in steps | increase in speed | decrease in time |
|---|---|---|
| 2 | 100% | 50% |
| 4 | 300% | 75% |
| 6 | 700% | 87.5% |

The image resolution in photopolymers is deteriorated by the effect of stray light which becomes more pronounced with increasing exposure time. A reduction in exposure time by more than 50% as demonstrated in the above tests effects a considerable improvement in quality of the manufactured product.
Taking into account the facts, that the photosensitivity of compounds B1 and B2 are clearly superior to that of compound A, this effect is highly appreciated in technique.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 18th day of November 2002

Hidetaka Oka

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